The Investigation of a Sample of Fluor Spar

by Chas. J. Robinson

1912

Offered as a senior thesis for the degree of Bachelor of Science, chemical engineering. - University of Kansas

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CONTENTS-OUTLINE

List of Illustrations. 3

Bibliography. 4

Discussion proper. 5

Cause of thesis. 5

Letters of inquiry. 5

Description and preliminary examination of fluor spar. 6

Appearance. 6

Treatment with dilute H_2SO_4. 7

Conversion to $CaSO_4$, quantitative. . . . 7

Examination for silica. 8

Explanations possible (Five) 9

(1) Silica. 10

(2) Sulphuric acid. 11

(3) Hydrochloric acid. 11

(4) An undiscovered element. 12

(a) Some new ideas in literature. . . 13

(b) Spectrum study. 13

a' Literature. 13

b' Preparation of pure SiF_4. . . . 16

1' First run. 16

2' Properties, purification, and literature. 19

a" Freezing and fractional distillation. 19

b" Absorption. 20

c" Purification of silica. . 20

c' Other runs and data. 21

d' Curve for spectrometer calibration 26

e' Run on fluor spar and data. . . 27

f' Comparative plot. 34

(c) Resume. 41

(5) A study of the acid made from the fluor spar, compared with other samples of HF..... 42

(a) Literature

a' Preparation. 43

b' Properties. 45

c' Analysis. 46

(b) Manufacture. 49

(c) Examination. . . . . .

a' Apparatus. 50

b' Titrations, data, observations . 52

(d) Results and conclusions. 56

(6) A different basis of measurement 60

Final Conclusions.

LIST OF ILLUSTRATIONS

Apparatus for generation of SiF_4. . . 17

Curve for calibration of spectrometer . . 27

Comparative plot of spectra. . . . . 35 - 40

Safety pipette. 51

Diagram of specific gravity - percent strength. 57

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AN INVESTIGATION OF
A SAMPLE OF FLUOR - SPAR.

About April 1st 1910 a letter was received at the university from Mr. Donald V. Liddell of the United States Metals Refining Co, Rosiclare, Ill. This letter contained in part the following:

"I desire to bring two things to your notice which may be of sufficient interest to you to have some of your students work them out.

The first is a quotation from a letter describing an interview with the maker of hydrofluoric acid (Mr. Erik Enequist once of Brooklyn, N. Y.)

He states that when using fluorspar from the Rosiclare Lead and Fluorspar Mining Co., Rosiclare, Ill., he was convinced that there was some new element present having a lower atomic weight than fluorine. This was found out because acid testing 19° B. showed 75% strength whereas the gravity would have indicated 60% strength. This particular acid was very fine for glass polishing, and he thinks in distilling, more of this element is obtained in the final product. If the acid is precipitated by $CaCl_2$ in the presence of an alkali, and the precipitate is washed and treated with concentrated HF, this new element dissolves out, but the fluorine does not. I suggest that you try this on general chemical acid as well as our own.

This letter forms the starting point at which this investigation began, and around which it centers. Subsequently considerable correspondence was necessary, but most of it of such a nature that I will save time by merely outlining its nature.

The first was a request for a sample of the fluorspar in question, and resulted in the obtaining of a sack containing about ten pounds of the mineral

ground to somewhere near one hundred mesh. Next I wrote to Mr. Liddell to learn if the irregularity was still observed (1911), to obtain if possible some of the abnormal HF, to learn as many more details as possible, and to learn the whereabouts of this Erik Enequist who reported the fact. I learned practically nothing, except that Enequist could not be found. Later I found his name in the Society of Chemical Industry Directory, and wrote to the address given, but the letter returned without reaching him.

I next attempted to find out by correspondence some of the commercial methods used by manufacturers and users of hydrofluoric acid to determine its strength. Only two or three satisfactory answers were received, and their methods were based on titration with standard alkali;- sodium or potassium hydroxid, with phenol-phthalein as indicator.

While waiting for replies on some of these letters I made a rough preliminary examination of the fluorspar with the following results: The mineral as received was very finely powdered, homogeneous, nearly pure white in color (very slightly grayish). Treatment with dilute sulphur-

ic acid caused no violent effervescence. There were some bubbles at first probably due to air enclosed between the particles of powder, and some collected on the sides of the test tube, but these were practically eliminated by wetting the powder thoroughly before adding the acid. I assumed then that the amount of CO_2 present as carbonates was very small.

Next followed a rough quantitative treatment with concentrated sulphuric acid according to the equation

$$CaF_2 \text{ plus } H_2SO_4 = CaSO_4 \text{ plus } 2HF$$

to determine the apparent combining weight of the fluorine present. The data was as follows:

Crucible.....	21.6533	grams
Crucible plus CaF_2 taken..	22.7745	"
CaF_2 used.....	1.1212	"
After slow heat	22.7733	"
Hottest Bunsen	22.7695	"
Blast lamp.....	22.7656	"
$CaSO_4$ plus crucible.....	23.5418	"
*Again.....	23.5453	"

Calculations for the above gave Calcium .55608 gms. and Fluorine.56512 gms. and a combining weight of 20.05 for fluorine. If I assumed that the last loss in weight on blasting was due to driving off of the CO_2 present as carbonate, then make allow-

ance for a part of the calcium being present as calcium carbonate instead of calcium fluorid, the combining weight of fluorine appears to be 19.6. Re-blasting the $CaSO_4$ precipitate for a long time and using the last weighing (the one marked with the star*) the combining weights calculated for fluorine were 19.5 and 19.3.

These values are all above 19.0, the accepted combining weight of fluorine, and give no indication of the presence of a similar element with combining weight lower than 19.0. (There is of course the possibility of the substance having been driven off under the blasting, though I assume all of that loss to be due to water and carbon dioxid).

Another sample of the fluorspar treated in the platinum crucible with chemically pure HF gave a slight loss in weight (material thoroughly blasted before and after treatment with HF).This loss probably caused by the conversion of silica present into silicon tetrafluorid according to the equation

$$4HF + SiO_2 = SiF_4 + 2H_2O.$$

This completed preliminary investigations and offered a starting place for the systematic

and more complete investigation. The following table arranged gave as nearly as possible all of the explanations which I could imagine for Enequist's problem.

(1) Silica present as impurity would behave as he has described, at least to some extent

(2) Sulphuric acid (because more of it is obtained in the final product in hydrofluoric acid manufacture.)

(3) Hydrochloric or hydriodic acid present in the hydrofluoric (because they too are halids)

(4) Some new and undiscovered element present in the spar, with lower combining weight than 19.

(5) That in titrating the HF in question he had used KOH instead of NaOH and that some error appeared due to the formation of a potassium salt entirely different from the corresponding sodium salt; or that some one of the impurities in the HF had a much greater effect in neutralizing one base than another.

(6) That he had used an entirely different method of determining the percentage strength of his acid, one of which I know nothing, and one which is considerably influenced by one or more of the impurities in the acid.

Then to take up each of these heads, giving each all of the consideration which it appears to be worth constitutes the work of the thesis.

(1)

Silica or hydrofluosilicic acid is one of the commonest and most abundant impurities in commercial hydrofluoric acid running from 2.7 % to 14.9 % H_2SiF_6 * but on account of its higher atomic weight than 19 it appears to be excluded on the start.

Acid of 19° B. which he states to have 75% strength, or ordinarily 60% strength corresponds to the specific gravity 1.152. The two tables which I was able to find in Dammer** and in Landolt and Bornstein*** give 40.0% and 48.0% acidity. for that specific gravity. Gmelin-Kraut* gives the same tables in part as are in Landolt and Bornstein, work done by Eckelt****** and Winteler*******. Dammer** gives 17.5 % as the acidity of fluosilicic acid at 1.1512 specific gravity. Apparently then, by no means of figuring can the admixture of silicon compounds raise the apparent acidity of the HF, even though it be present in very large quantities.

*Gmelin-Kraut page 17 Fluor.
For * ** *** etc. see the complete references in Bibliography of this paper.

(2)

Sulphuric acid likewise ranges from 0.8% to 4.0% in commercial HF (Gmelin-Kraut) and more of it is obtained in the final distillation,,- but again it seems impossible to figure theoretically how any percentage of sulphuric, even though it is a dibasic acid can raise the percentage without a large increase in specific gravity. Dammer again (page 146 of the Physical Tables) Landolt and B°rnstein and Van Nostrand's Chemical Annual, give sulphuric acid of 1.151 specific gravity an acidity of slightly over 21. %.

His statement as to the dissolving out of the material in HF is hardly applicable either to $CaSO_4$.

(3)

Any of the other hydro-halogen acids are similarly excluded because of the greater molar weight.

As a simple verification of my statements under (1), (2) and (3) I took chemically pure HF from the stock room, diluted it to 1.151 specific gravity and titrated with approximately half normal sodium hydroxid. One pipette full required 104.75 (a) and 105.10 (b) cubic centimeters of

the alkali. Then I prepared a mixture of the pure HF with H_2SiF_6 and titrated again. This time a pipette full required only 92.50 and 92.10 c.c.; a very distinct loss in acidity.

(4)

The preliminary tests gave quite good evidence that if a new element existed in the fluor spar, it was not present in sufficiently large quantities to affect a quantitative analysis of the CaF_2 - $CaSO_4$ type to a marked degree. Some reading and inquiry brought to light the conclusion that an analysis for silica in the presence of fluorids, or fluorids in the presence of silica would necessitate the use of special precautions and special methods. Furthermore, the most of these special methods demanded the use of platinum apparatus which was entirely out of the question; so the course finally followed was, at the suggestion of Dr. Cady, a study of the spectrum, reasons being the availability of excellent apparatus, the extreme delicacy and sensitiveness of the method, its thoroughness in not allowing any of the material to escape during the experiment, and its conclusiveness in naming the identity of the elements found.

The fruitfulness of a complete investigation of this line, with a view to finding a new halogen, encouraged by the finding of the following quotation from Werner (New Ideas on Inorganic Chemistry) page seven "It can therefore be deduced that in the hydrogen-helium series the mean difference is about 1.5, so that in this series it is very probable that an element is to be be expected, possibly the prototype of the negative elements.

and on page 10,

"Finally when we assume as Mendelejeff* has done, that a metalloid element is wanting in the hydrogen series,.....

"*Note:- On reading Walden's obituary notice on Mendelejeff (Chem. Zeit., 1907), the author became aware for the first time that Mendelejeff had predicted that a new element of the halogen group would be found with the atomic weight of three."

The best work upon fluorine and its compounds which I was able to find was the volume "Le Fluor et Ses Composeès" by Moissan. This describes a condiderable amount of spectroscope work on several fluorine compounds as well as fluorine itself, and I quote some of his data.

Salet before Moissan compared the spectra of silicon fluorid and silicon chlorid and determined lines belonging to fluorine as follows:

F Alpha	1	692	
	2	686	about
	3	678	
F Beta		640	
F Gamma		623	

Moissan used a number of gases more or less dissociable under the electric spark under high temperature. Silicon and carbon fluorids which do not attack silicates were examined in ordinary glass tubes, fluorine and hydrofluoric acid required special platinum apparatus. His results for silicon tetrafluorid together with those of Salet are

Moissan	Salet
734	
714	
691	692
687.5	686
685.5	
683.5	
677	678
656.2 hydrogen	
640.5	640
634	
623	623
598 SiF	

The silicon tetrafluorid, Moissan says was absolutely free from HF vapor. After the spark had passed for many hours a slight deposit of "gris de silicon" was produced on the surface of the glass. Baly states that silicon tetrafluorid behaves much like cyanogen, and that cyanogen

soon polymerizes to paracyanogen, a brown solid in the spectrum tube so that it is necessary to use an end on vacuum tube to prevent the obscuring of the illumination. The current will pass for only a few minutes owing to this rapid polymerization, so that if it is desired to measure or photograph the spectrum it is necessary to arrange the apparatus so that it can be refilled. I do not assume that Baly means to state that silicon tetrafluorid polymerizes, merely that it causes a similar darkening of the tube, or that it disappears.

Moissan examined the tri and pentafluorids of phosphorus, and carbon tetrafluorid. This latter was the most beautiful obtained, contained many lines, and the fluorine lines were very brilliant. He prepared carbon tetrafluorid in five ways.

(1) By the action of fluorine at low temperatures upon carbon.

(2) By the action of Fluorine on CCl_4.

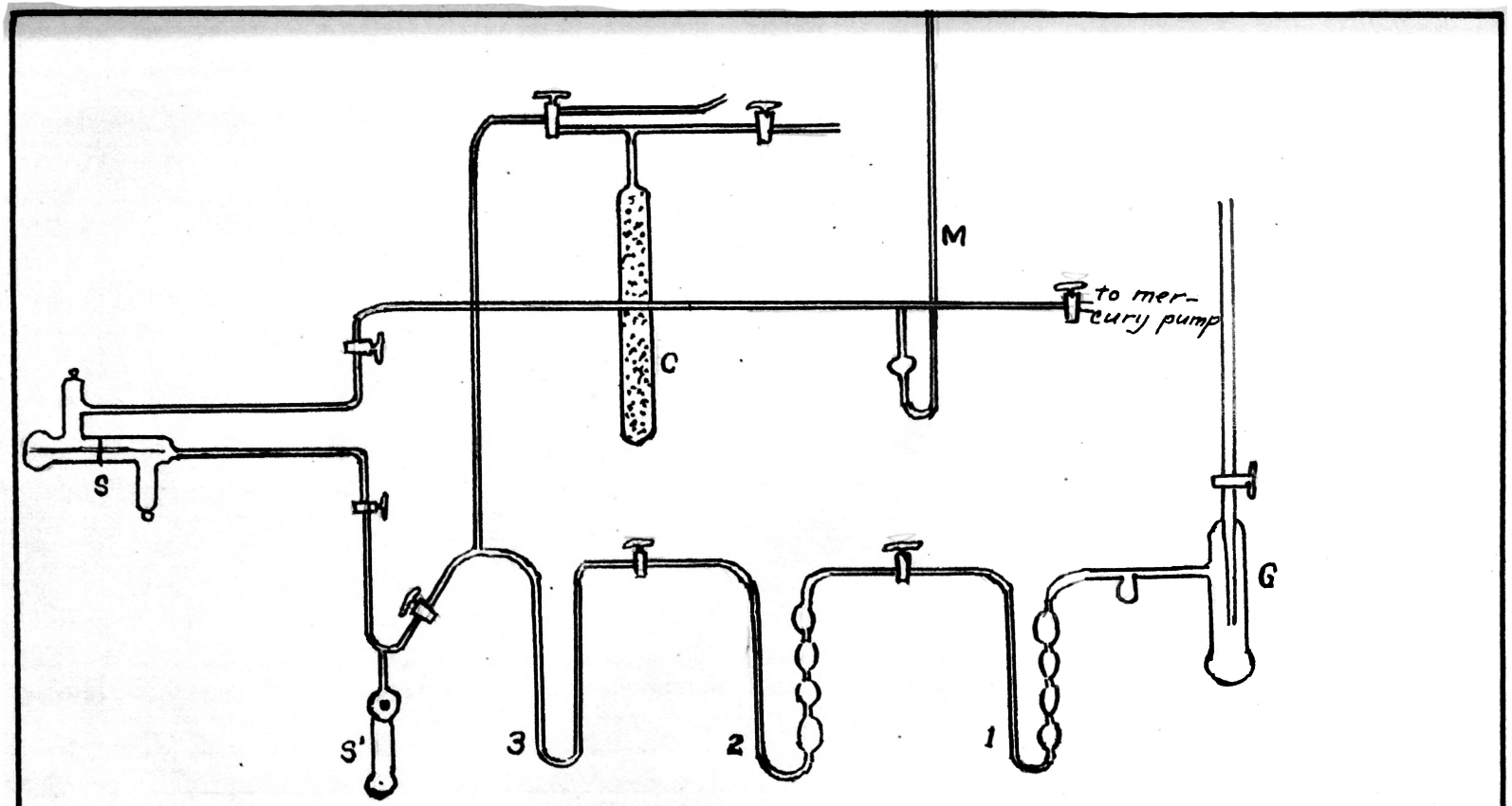
(3) By the action of fluorine on $CHCl_3$.

(4) By the action of Fluorine on Formène.

(5) By the action of silver fluorid on carbon tetrachlorid vapor.

Considering the material on hand (I could find only one small bottle of pure KHF_2 at hand) it was decided to make the examination upon silicon tetrafluorid, with the hope of finding the stranger somewhere in the process. The scheme was to prepare pure silicon tetrafluorid from the potassium hydrogen fluorid on hand, make careful readings on its spectrum, then to prepare it from the fluorspar in question and make similar readings and compare with the pure.

I placed a mixture of one or two grams of potassium hydrogen fluorid with ten or twelve times excess of powdered sand in the glass generating flask of the apparatus shown, applied a flask of frozen mushy chloroform to the first bulb or condensing tube, another of liquid air to the second and still another of liquid air to the third. Next, or preferably before applying the liquid air tubes, all of the gas (air) is exhausted from the apparatus by means of the mercury pump, and the reaction is started by admitting a small amount of boiled sulphuric acid through the stop cock tube. The frozen chloroform at about -70°C. froze out the water vapor, but allowed the SiF_4 to pass on (B.P. of SiF_4 is -90 to -97,- Gmelin-Kraut 67)



G - Generation flask or bulb.

M - Manometer tube.

C - Charcoal absorption bulb.

S and S' Spectrum tubes.

1 - Condensing bulb surrounded by mushy frozen chloroform.

2 and 3 " bulbs " " liquid air.

SILICON TETRAFLUORID APPARATUS.

over into the bulbs cooled with liquid air, where it condensed in the first. From here it was fractionally distilled into the last bulb so as to effect a better separation. This was done by removing the liquid air bulb and allowing the condensing bulb to warm up slightly. The vapor given off was of course re-condensed in the last bulb, and whenever some of it was needed in the spectrum tube, the proper stop cock was opened, the last liquid air bulb removed, and enough of the contents of this bulb allowed to vaporize to give a good spectrum. This last step required only a minute or two at the most. Too low a pressure will not allow enough current to pass to give a spectrum; and similarly too much pressure will produce the same result. The proper pressure is considerably less than one millimeter, though I do not know it exactly, and was produced in two ways;- by a mercury pump shown in the accompanying plate, and by a bulb filled with cocoanut charcoal, and cooled with liquid air, this also shown in the drawings. Manometers and the other details of the apparatus are shown in the drawings and need no further explanation.

Two spectrum bulbs were connected with the

apparatus; one on which the observations were made and one which might be sealed off at any time so as to preserve a permanent sample. This latter provision I afterward found to be useless, as the two which were sealed off became entirely useless after fifteen minutes sparking, due to the rapid decomposition.

When finally the lowest boiling fraction of the first run was admitted to the spectrum tube it was found to contain considerable carbon dioxid. Spectrum lines not belonging to carbon were apparent, and they no doubt belonged to fluorine, but for further search it would be essential to remove the carbon.

We then tried to separate the carbon dioxid from the silicon tetrafluorid by inserting in place of the last liquid air bulb a bulb of liquid methane (natural gas), designed to freeze or condense out the carbon dioxid, allowing the SiF_4 to pass by, but the effect was hardly noticeable. After each of these attempts at purification, the gases in the spectrum bulbs were pumped out with the mercury pump, or later with the charcoal bulb, and a fresh fraction admitted.

Since the potassium hydrogen fluorid was pure

the sulphuric acid was boiled to remove CO_2 and air, and the sand was of somewhat questionable origin and composition, the CO_2 was no doubt due to carbonate in the sand.

The next question was: could I absorb the CO_2 without disturbing the SiF_4? Silicon tetrafluorid in the presence of the least water forms H_2SiF_6 in a jelly like mass, and the two are not easily separable. This excludes solutions such as KOH, $Ba(OH)_2$, and NaOH. Lime glows in the gas, so vigorous is the reaction. Dry alkali earths and metallic oxids absorb it with heat. In short I could find no convenient absorption method for effecting a separation, and was forced to the preparation of chemically pure silica. This I accomplished by treating water glass with hydrochloric acid, evaporating to dryness, heating at 120°, redissolving the soluble, treating with hydrochloric acid again, and evaporating as in the ordinary quantitative analysis for silica, and finally adding H_2SO_4, evaporating to white fumes and washing thoroughly. The last treatment with sulphuric acid was to remove all chlorids and prevent their appearance in the spectroscope

The second run, using the purified silica in place of the sand resulted better. The first fraction contained some CO_2, but by three or four fractionations I was able to boil off all of the carbon, and obtained a fairly distinct F spectrum. The assumption would be then, that the mixture of CO_2 and SiF_4 was non homogeneous. Both seem to be in the solid condition and to sublime upon warming. Probably each substance exerts its own vapor pressure, and tends to distil over separately and independent of the other,- two phases being present. From a solution of the two gases or a solution of CO_2 in solid SiF_4, if such a thing were possible, the gas present in larger quantity would tend to pass off first and most easily, with the vapor pressure of the solution. But here evidently the CO_2 present in least quantity passed off first, for the reason that each substance or phase has its own vapor pressure acting independently, and in the two efforts to vaporize the one present in the least quantity passes off first. (See Walker, page 85).

A number of readings of the lines exhibited were made covering each fraction of the supply,

and later the apparatus was recharged and other series run. All of the fluorine lines lie at the extreme red end of the spectrum, and are very difficult to see and measure. In fact I was not able to locate all of the lines which Moissan assigns to fluorine (six out of twelve), and after repeated trying came to the conclusion that he must have used photographic means for their detection. Many obstacles interfered with the work: prolonged sparking soon decomposed the gas upon which measurements were being made, so that it grew fainter and fainter; the heat also brought forth from the glass quantities of hydrogen which quickly obscured the fainter fluorine lines. This was best removed by heating the tubing with a bunsen, admitting a small quantity of air as a sort of flushing agent, and pumping out the air with the hydrogen. Early in the work the barrel of the mercury pump became roughened (possibly etched by a trace of hydrofluoric acid) and it was necessary to replace the barrel and add to the apparatus the charcoal bulb already described. Form time to time local leaks of air required attention, but I finally

obtained enough data to serve the purposes. They are as follows:

Magnitude	Color	Turns	Wheel
Run #6R			
2 *	Red	1	1.2
5		1	2
5		1	4.35
5		1	4.81
3		1	5.85
3		1	7.4
4		1	10.9) b
4		1	11.25
4		2	0.1)
4		2	0.27)b
3-4		2	1.31
3		2	2.1)
3		2	2.29)b
3		2	3.64)b
4		2	5.94 b
4		2	6.3
3		2	7.9
4	Yellow	2	8.68
4		2	11.25
5		3	0.05
		3	1.55
2-1		3	3.4
2-1		3	4.3
Run #7R			
1	Red	1	1.19
4		1	5.82
4		1	7.39
5		1	10.39
4		1	10.79
5		1	11.71 O)
			11.62
4		2	0.31
4		2	1.34
3		2	2.10
4		2	2.99
5		2	4.45 b

*Note: Magnitude I have indicated by the figures 1,2,3,4,5,6, ranging from 1, the strongest to 6, the faintest visible line. "b" indicates a rather indeterminate band of color of the width indicated.

Magnitude	Color	Turns	Wheel	
5	Red	2	6.47	b
5		2	9.00	b
1	Yellow	3	3.39	
1		3	4.29	
Run #8R				
1	Red	1	1.2	
3-4		1	5.88	
3-4		1	7.40	
3-4		1	10.81	
5		1	11.67	
3-4		2	0.24	
4		2	1.32	
3		2	2.11	
4		2	3.08	
Run #9R- Pumping out				
1		1	1.21	
1-2		1	6.70	
1		1	7.41	
2		2	1.8	
2		2	3.7	
3		2	7.89	
3-4		2	8.74	
4-5		2	11.38	
4-5		3	0.12	He?

Observations made on carbon in order to have its location, for purpose of identification in the future:-

	Red	2	4.20	shading
	Green	3	11.5	"

and many others.

Same made on helium:-

	Red	0	1.29
	"	0	10.22
	Yellow	3	0.00

Same made on hydrogen:-

(c)	Red	1	1.25
(F)	Blue	7	1.10
(G')	Violet	12	70

Run 10R

Magnitude	Color	Turns	Wheel	
	Red	0	46	
:		0	46	
L				
:		0	54	
:				
:		1	10	
:			11	
:			10	
:		1	67	
:			74	
:			74	
all		1	108	
very			108	
faint				
:		2	26	
:				
:		2	415,	
:		2	805)	b
:				
1	Yellow	3	34	Mercury
1		3	43	"
5		3	82	
5	Green	4	45	b
4		4	775	
4		4	90	
5		5	83	
5		5	97	b Carbon ?
4		5	105	

both of these last two lines shade gradually off, having the appearance of that characteristic carbon banding.

	7	64
	7	84

from this point on, most of the lines become so broad in the spectroscope that the location is somewhat indeterminate,- approximate.

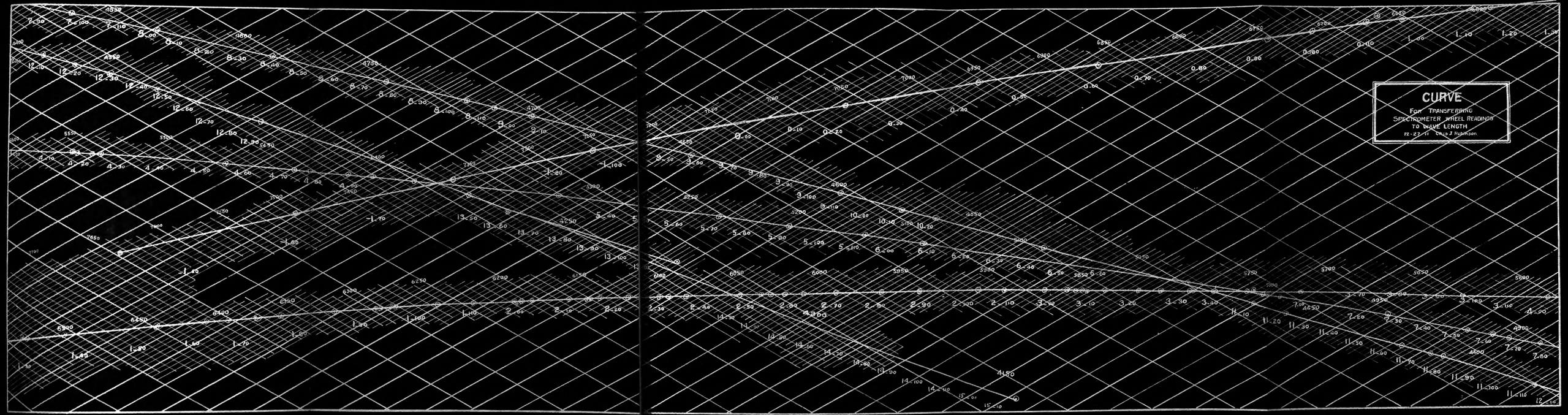
9	101

The first of a series of graduated bands increasing in brilliancy toward the violet end of the spectrum. Each member of the series begins sharply at the point of measurement and shades off to nothing toward the violet.

	Turns	Wheel	
	10	185	second
	10	68	third
	10	107	
	11	70	
	12	31	
	12	44	
	12	71	
	12	129	
	13	47	
	13	89	
	14	64	
5	16	0	
4	16	62	
(read helium as a check)			
	2	119.5	
apparatus pretty warm			
another trial	1	66	
	1	75	
air in apparatus			
again	0	44	
again	0	05	
(very uncertain if I saw this at all)			

Now to transfer these spectroscope readings to standard wave length figures or Ångström units * it was necessary to calibrate the spectroscope or spectrometer as it should properly be spoken of. For this purpose I plotted the curve which accompanies this paper using several hundred measurements made by Dr. Cady with the instrument upon

(*Note, an Ångström unit is one ten millionth of a millimeter.)


CURVE
FOR TRANSFERRING
SPECTROMETER WHEEL READINGS
TO WAVE LENGTH
12-27-11 Chas J Robinson

argon, helium, neon, and hydrogen. The device of using 60° coordinates prevents the spread of the curve over so much vertical distance, and the breaking into five sections is for the same purpose as well as to save in length. The coordinates are spectrometer wheel readings with their fractions against wave length or Ångström units.

Next I loaded the apparatus with fluor spar and began a series of measurements upon the SiF_4 manufactured from it. To my surprise, almost no CO_2 appeared in the spectrum, even at the very first, and a number of good readings were possible. They are as follows:

Run 11R

Magnitude	Turns	Wheel
5	0	14 15 16 17
6	0	34
6	0	48 478
5	0	575 57 573
6 ?	0	76 73
6 ?	0	97
6	0	116 b
3	1	12

Magnitude	Turns	Wheel	
6 ?	1	37	
6 ?	1	558	
	1	555	
	1	565	
4	1	665	
	1	651	
3	1	737	
	1	731	
adjusted cross hair then read on hydrogen-helium tube for purpose of checking			
3	0	125	
		135	
3	0	104.0	
		104.	
	1	142	
	2	17	
1	3	01.)	
	3	01.)	Helium

Run 12 R with adjusted cross hair.

6	0	12.4	
3	0	103.5	
1	1	14	
5	1	42	
	1	58.4	
5	1	875	
shading off to			
	1	122.	
6	2	1.8	

many others fine and cclose together.-- Hydrogen in apparatus.

then for check:			
1	3	00	Helium

Run 13 R After flushing hydrogen out of the apparatus as well as possible and

distilling in a second fraction. All lines rather dim, and I measured only the more distinct ones.

Magnitude		Turns	Wheel	
6		0	097	
		0	26	
6		0	633	
		0	562	
5		1	11	
		1	082	
4		1	74	
		1	74	
4		1	108	
		2	42	b
2		3	345	
		3	342	
2		3	425	
		3	431	
		3	431	
5		3	875	b
5		3	127	b
5		4	077	b
6		4	44	b
2		4	71	
		4	71	
5		4	1087	b
	here begins another of those series of banded spectra already described, and which I think is characteristic of silicon tetrafluorid.or carbon.			
6		5	442	b
5		58	103	b
6		6	75	b
6		6	104	b
6	Green ?	7	199	b
6		7	508	b
	same line	7	52	b
6		7	83	b
6		7	114	b
6		8	091	b
6		8	30	
	this begins a slightly different series in the violet SiF_4 I think.			

Magnitude	Turns	Wheel
5	8	1083 b
5	9	44 b
5	9	62 b
5	10	175 b

air in apparatus

Run 14 R third fraction

Good clear spectrum (Direct current)

5	0	156
	Ω50	150
		19
		18
5	0	45
		45
5	0	567
		60
		55
6 ?	0	631 ?
6	0	77 b
6 ?	0	945
4	1	122
		124
5	1	55
		545
		553
		54
6	1	59
		59
5-6	1	67
		68
		678
	67	67
		679
		67
3-4	1	748
		745
5	1	109
		108
		110
		109 b
6	2	02
		03
6	2	134
		136

Magnitude	Turns	Wheel
5	2	218
		21
6	2	301
		30
		30
6	2	44
6	2	661
6	2	92
6	2	125
1	3	35 Hg
1	3	44
		438
5	3	854
or two separate at	3	822
	3	87
4	4	03 b
1	4	716
		708
		704
4	4	111
		1112 b
6	5	488 b
6 ?	5	90 b
5	5	106 b
6	6	788
		80
6	6	868
6	6	1048
6	7	157 b
6	7	53
5	7	627
		637 Hg
5-6	7	788
5-6	7	85 b
5-6	7	109 b
5-6	7	117 b
6	8	227 b
6	8	30 b
6	8	45 b

somewhere about here the first suggestion of the bands previously mentioned begins

Magnitude		Turns	Wheel	
6		9	56	
			55	
6		9	102	
	measuring the violet side of the band			
5	"	10	25	
5	"	10	70	
5	"	10	1053	
4	"	11	295	
6		11	40	line
4	"	11	727	b
5		11	809	line
3	"	11	110	b
6		12	059	line
2	"	12	324	b
	possibly double			
1		12	45	line
6		12	708	b
6		12	1105	b
6		13	455	b
6		13	90	b
6		14	77	b
6		15	322	b
6		16	05	
6		16	63	

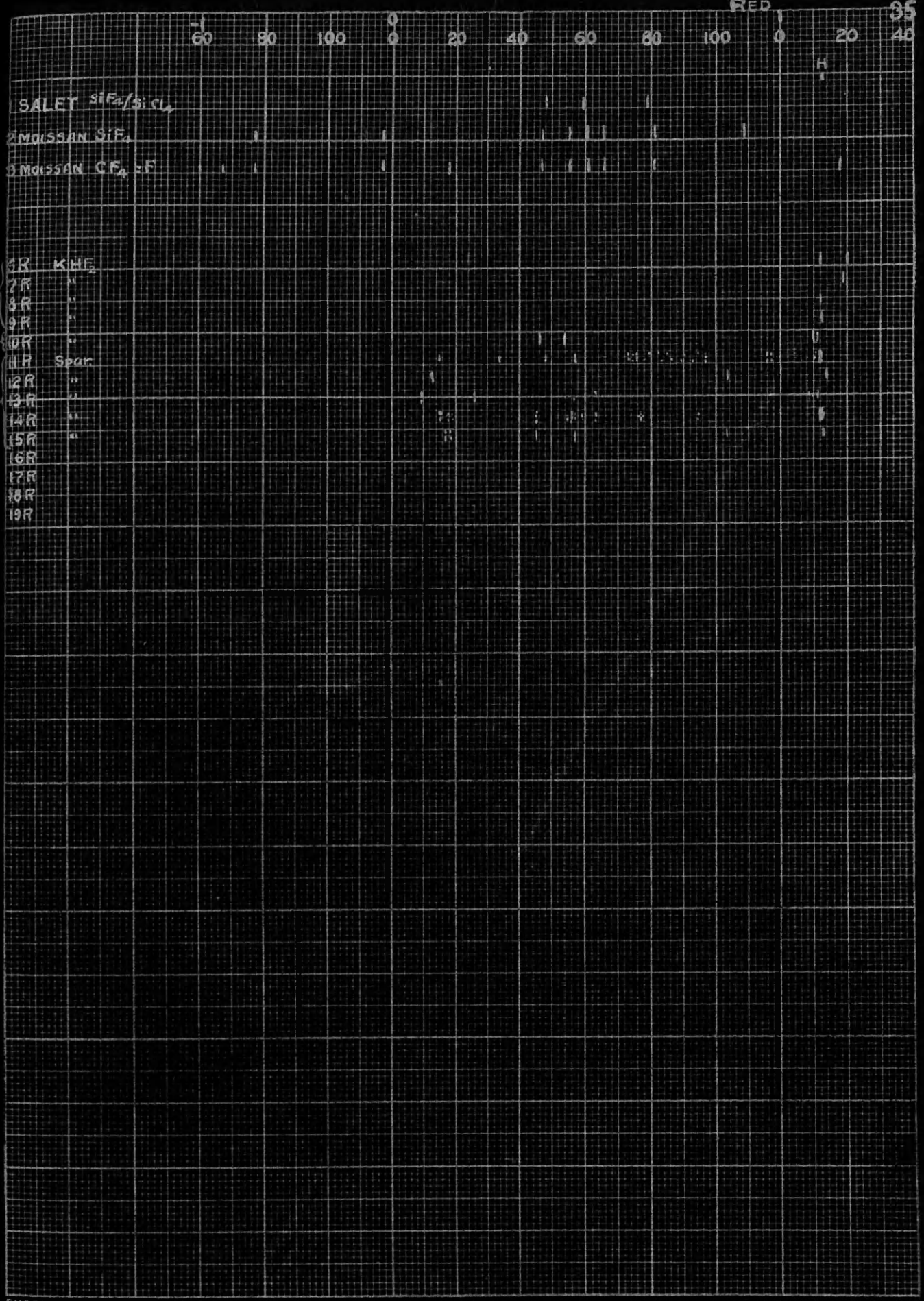
Run 15 R (another Sample) (Direct Current)
after some sparking, reading larger lines only

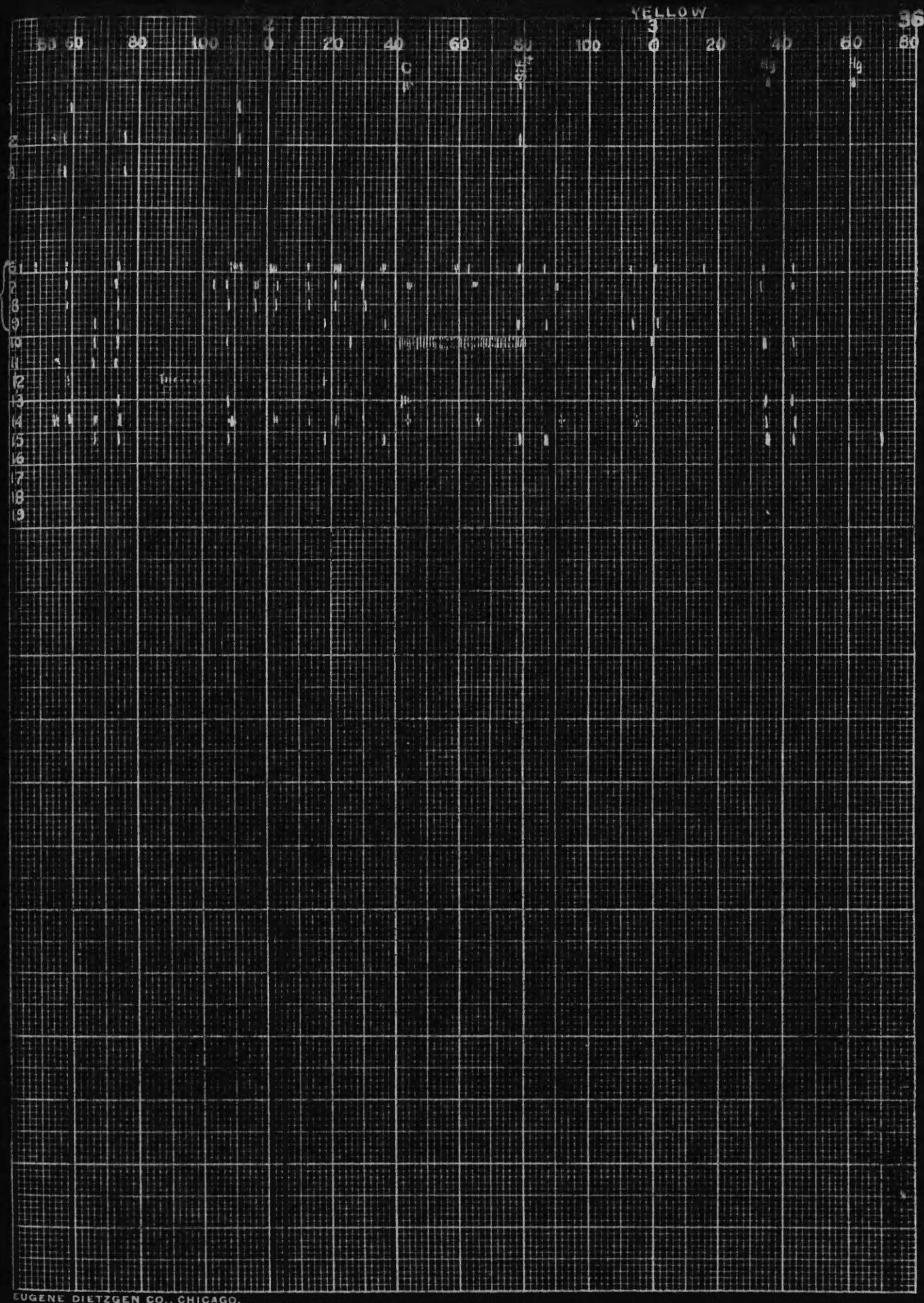
		0	165
			185
		0	45
		0	57
		0	1035
2		1	13
2		1	67
1		1	74
3		1	108
3		2	18
4		2	365
3		2	792
	orange		
3		2	872

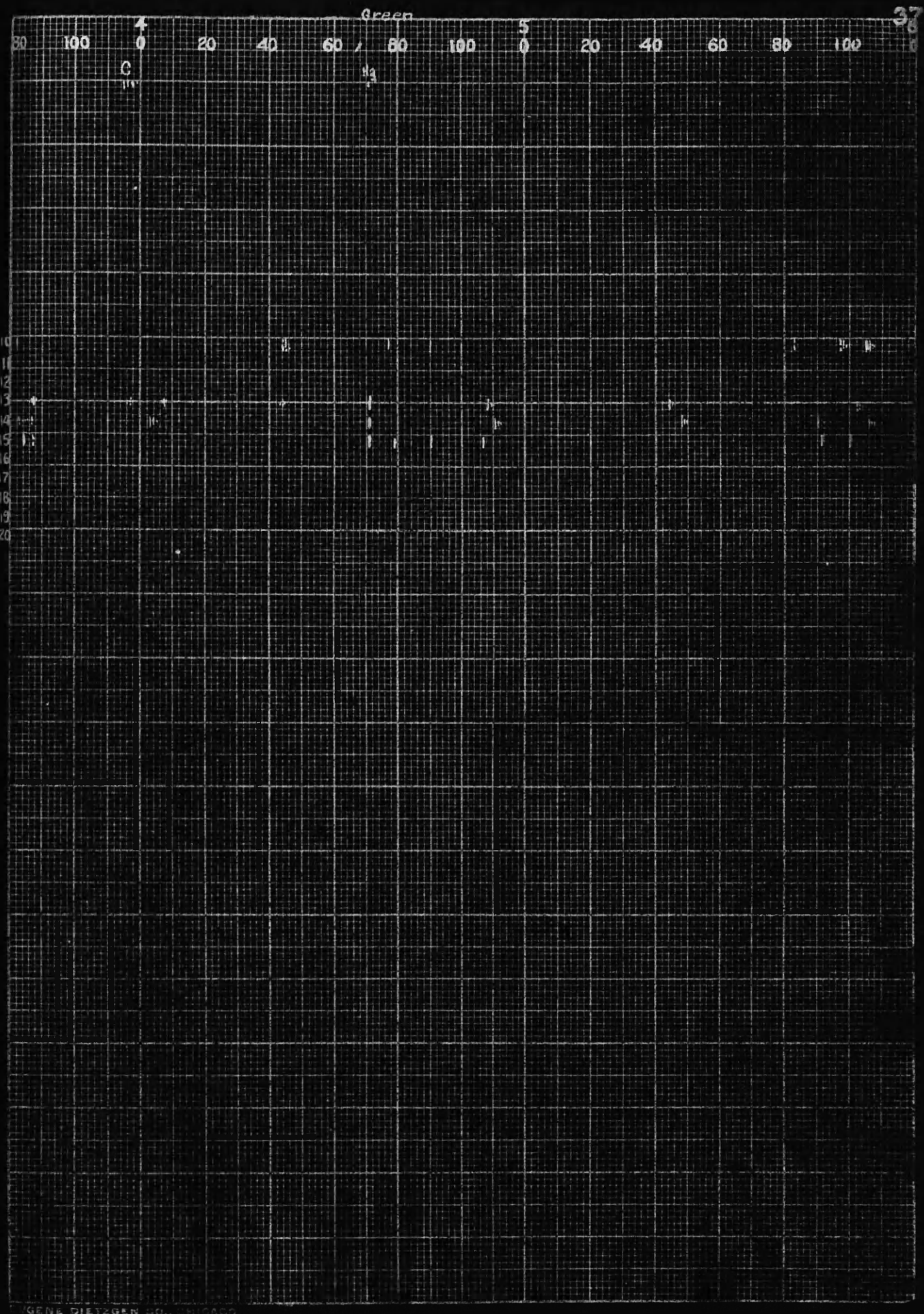
Magnitude		Turns	Wheel	
½		3	35	
1		3	431	
5		3	70	
5		3	84	
5		3	87	
1	Green	4	706	
3		4	795	
4		4	905	
5		4	1073	
5		5	905	
6		5	100	
6		6	241	
6		6	486	
5		6	621	
2		6	787	
3		6	895	
6		7	019	
5		7	631	
			621	
5		7	728	
5		7	795	
6		7	1097	
5		8	243	
4		8	325	
4		8	455	
6		8	64	
5		10	294	bands as before
5		10	445	line
		10	70	b
		10	109	
		11	3	
		11	765	b
		11	1101	b
		12	286	b
		12	45	
		15	34	
		16	04	
		16	66	

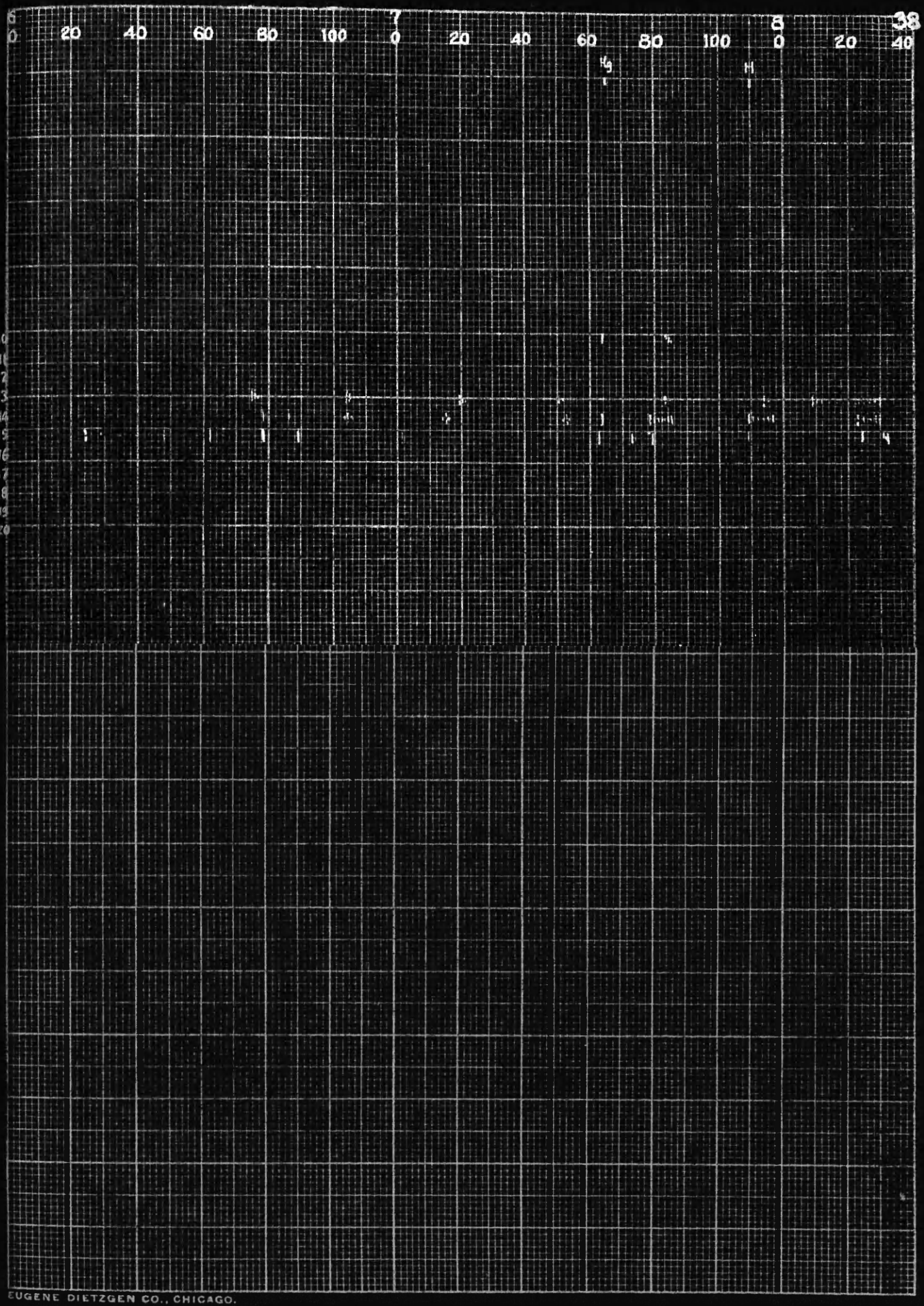
Next in order to better make intellegent comparison of the pure SiF_4 spectrum with that obtained from the fluor spar, and also to compare the two series with the theoretical or established lines; I plotted on cross section paper a chart of all the readings taken in the course of the work, and with them the SiF_4 spectrum of Salet, and the SiF_4 and CF_4 spectra of Moissam (Moissan's CF_4 spectrum is the same as that assigned by him to fluorine). In this chart I have made some attempt to indicate the banding, and to proportion the weight of the lines to the magnitude or brightness of those of the spectra, the very faint ones being represented by dotted lines, and vice versa.

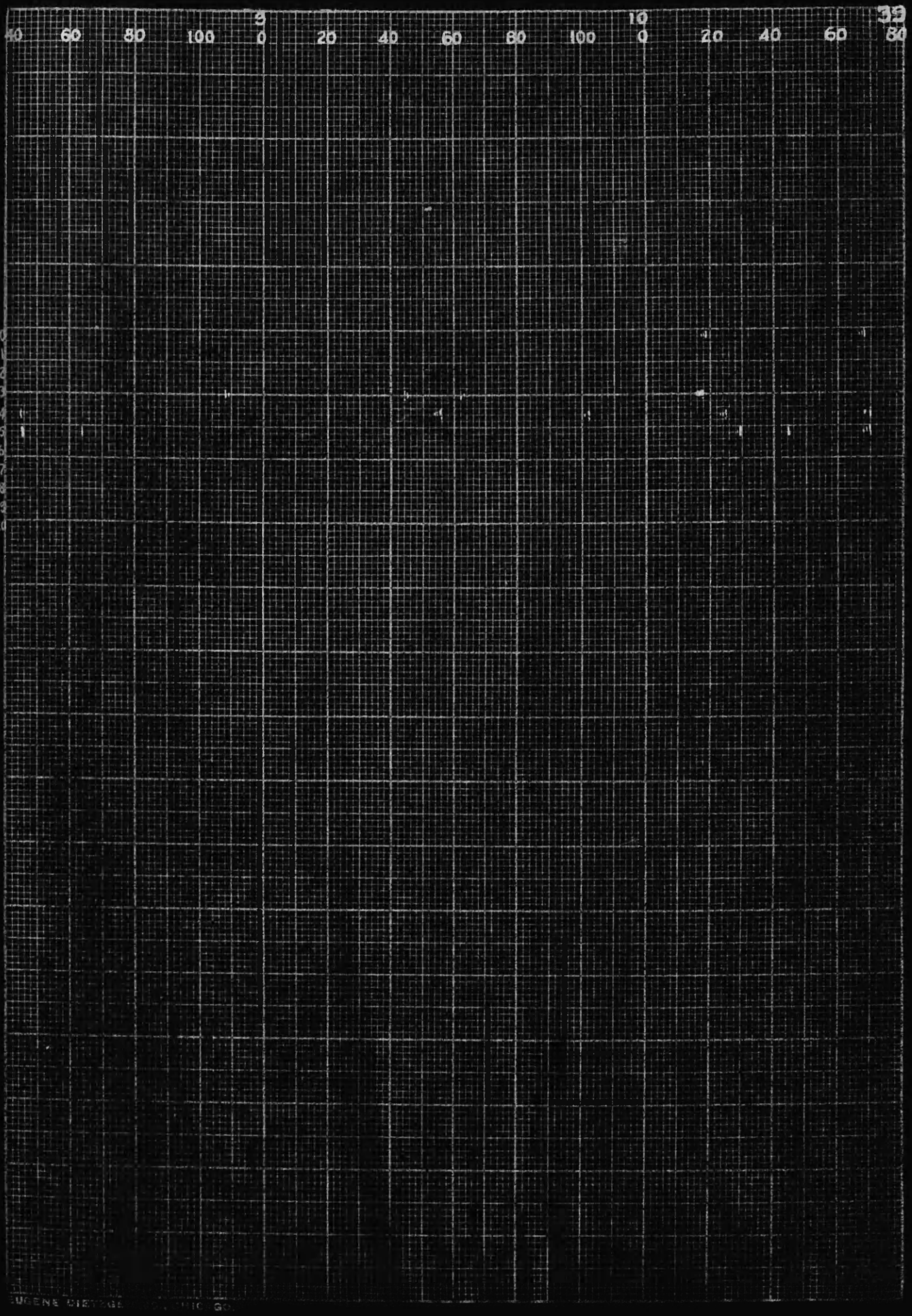
An inspection of the chart will show that all of the lines of Salet were found, with possibly the exception of 678 in both the pure SiF_4 and in the gas generated from the fluor spar. 678 is possibly present in the fluor spar, but not in the pure? Nine of the twelve lines of Moissan were found, and the three missing are so far to the deep red end of the spectrum that I could not see traces of any lines at all, and think it not

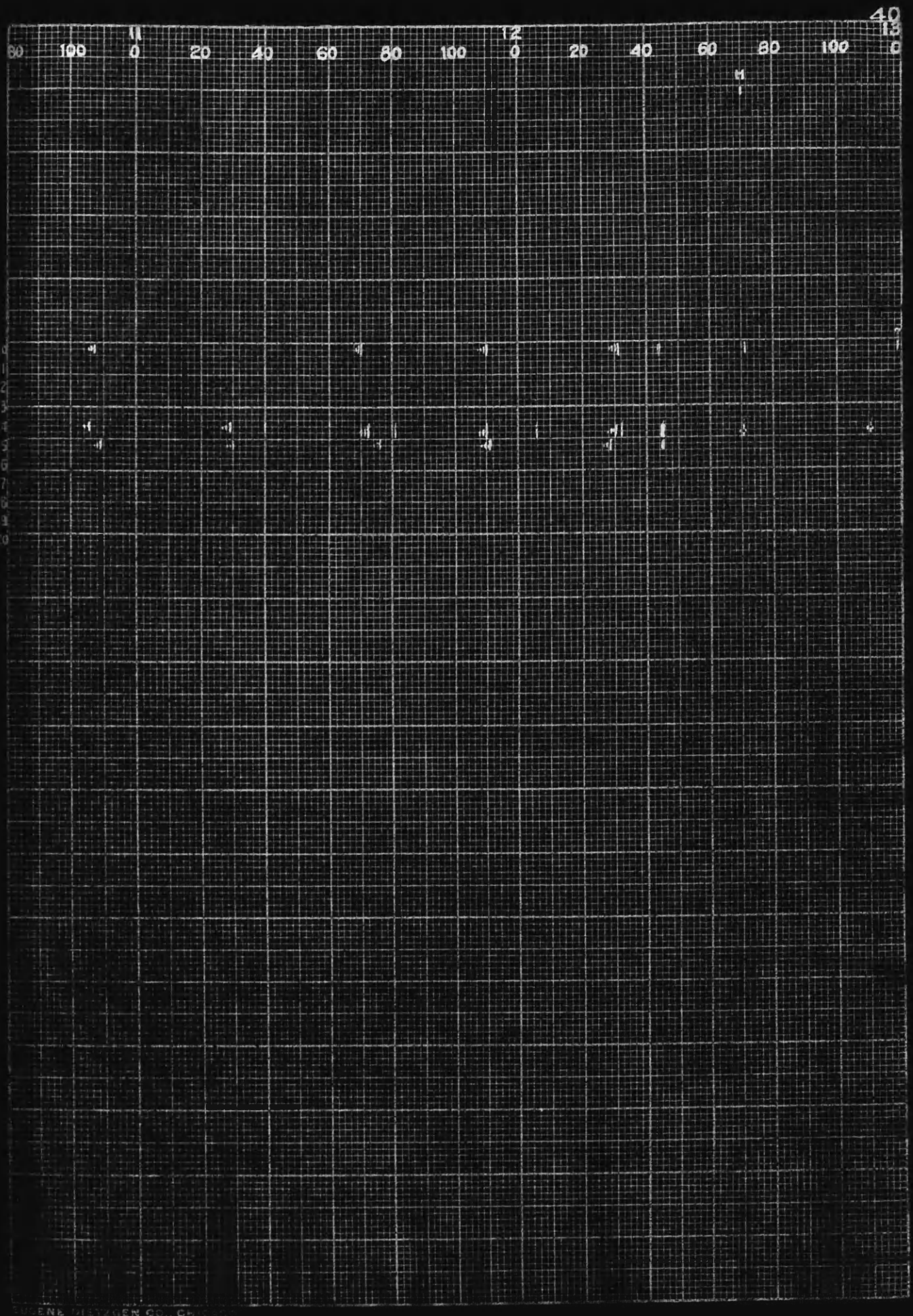





Green
37
4
5
80 100 0 20 40 60 80 100 0 20 40 60 80 100
C




9
10
40 60 80 100 0 20 40 60 80 100 0 20 40 60 80
10
11
12
13
14
15
16
17
18
19
20


11
12
13
80
100
0
20
40
60
80
100
0
20
40
60
80
100
0

unlikely that he may have used the bolometer or the photographic plate for their detection. The consistent banding in the violet, noticeable in # 10, #14, and # 15, is , I believe, ascribed to silicon tetrafluorid compound. In short the two spectra (the one from pure SiF_4 and the one from the fluor spar) are consistently alike. Nearly all of the non-fluorine lines are due to hydrogen, a few to mercury, and a few to carbon and air; but if appearing consistently in either, they appear consistently in both, showing rather convincingly that there is no trace whatever of a stranger in the gases evolved from the fluor spar. The possibility of its remaining behind, or of its not affecting the spectroscope is very doubtful. The improbability of the substance being condensed by the frozen chloroform is shown by the following table.

Substance	State	Melt P.	B.P.	Mol. Wt.	C.W.
SiI_4	Solid	120.5	290	534.46	127
$SiBr_4$	Liquid	-12.0	148	348	80
$SiCl_4$	Liquid	-20.0	59	170	35.4
SiF_4	Gas	-102.6	subl.	104	19
SiX_4	Gas?	?	?	?	2.5

If the new substance belongs to the halogen family, as we have assumed, its position in the table calls for a melting and boiling point somewhat below -100° C., unless it is, like hydrogen, a sort of prototype, and different from everything of its vicinity.

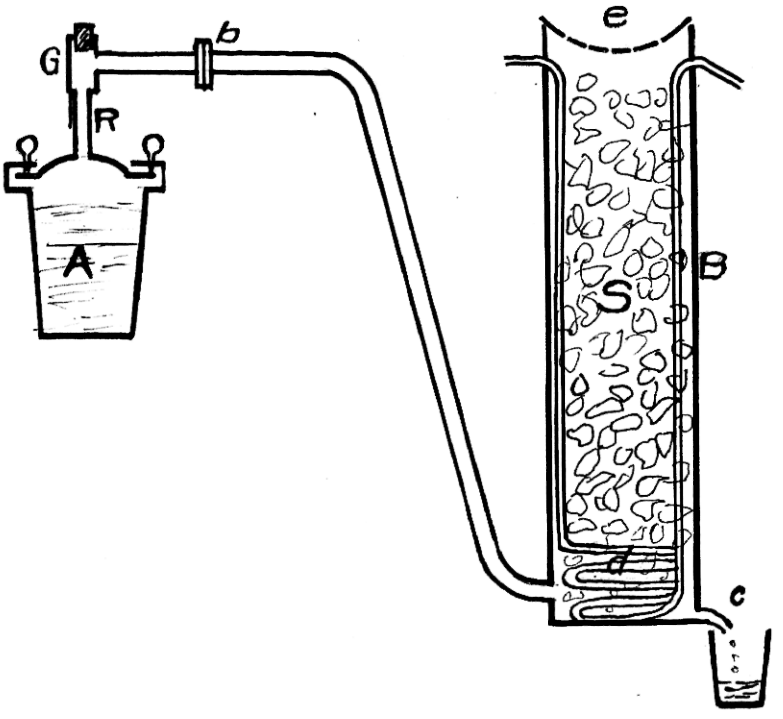
The results of the search by means of the spectroscope gives entirely negative results. It seemed perhaps a trifle strange that I should be able to get a more complete fluorine spectrum from the fluor spar than from the pure potassium salt, and the point caused a little reflection. I finally ascribed it to increasing proficiency in handling the apparatus.

(5)

The fifth possibility, that of an error arising from interchanging of KOH and NaOH solutions or the formation of an abnormal insoluble salt in the titration, demanded an examination, direct, of the hydrofluoric acid made from the fluor spar, and another set of apparatus. The fact that hydrofluoric acid attacks glass and all silicates called for a study of the properties of the acid, and the methods of manufacture

and purification.

The representative technical apparatus for generation of HF is described in Dammer (Tech) Volume 1, page 533., and is best described by the following figure



A. Cast iron pot with clamp connects through
R - A 10 M.M. gas pipe with
G - An iron outlet tee closed with a cork.
b - Is the joint between iron and lead piping to
B - The lead absorption cylinder.
e - A sieve-like arrangement admits water to B.
S - A packing of charcoal over which the water trickles slowly, absorbing the rising gas , and passing out at "c" into the lead cup.
d - Is a lead cooling worm, conducting water.

I wrote to Mr. Liddell to learn if this was the apparatus in common use. His reply confirmed this and gave the additional information as th the charge and mode of operation. Finely ground spar (100 mesh) is thoroughly mixed with sulphuric acid and placed in the retort, and a thin cover of fluor-spar put over the surface. The amount of sulphuric acid used is the theoretical quantity required to decompose 99% of the spar, including the covering. Two or three condensers are placed in series, and weak HF solution is used as the absorbing medium, it being much more efficient than pure water. Toward the last of the run the absorbing system is changed, as the gas coming over is likely to contain a larger percentage of H_2SO_4. The first acid is the best quality. In commercial practice the acid in the second condenser is usually used to put in the first next time, the third in the second and so on. The commercial acid is very impure, containing silica, sulphuric acid, and solid matter in solution, as will be more fully treated later.

Gmelin-Kraut states that the hydrofluoric acid bubbles out of the paste without the application of heat, so that most of it is out at the end of a few days. If the fluor spar contains, as it often does, silica,- SiF_4 passes over with the HF; this in the presence of water forms H_2SiF_6. It may be precipitated by dropping in KF or KOH (as K_2SiF_6) from which decant and distill to purify. If the fluorspar contains lead glance, then SO_2 and H_2S are also formed. The usual constituents of commercial HF are given by the following table:

	Gmelin-Kraut from	Sutton, Aver. #1	Volumetric Avg. #2
HF %	39.6 to 54.2	48.00	45.80
H_2SiF_6	2.7 to 14.9	13.05	9.49
H_2SO_4	.8 to 4.0	4.07	3.23
H_2SO_3	.5 to 2.0 (Sutton)	.49	1.06
Solid (after evaporation)		.16	---
Water (by difference)		34.23	40.42

The purified commercial acid sold as C.P. has a percentage HF of about 45 and a specific gravity of about 1.168,

It is constant boiling at 120° giving a 36-38% solution. The specific gravity indicates at 100° a molar weight of 20 corresponding to the formula HF, at 30° H_2F_2 represents the molar formula, and below this temperature, even higher molar weights are indicated. In solutions of ordinary concentration H_2F_2 is the molar weight formula, in dilute solutions HF. Anhydrous HF is made by heating KHF. The pure acid solution produces clear marks on glass, gas containing soluble fluorids (white acid) gives a matt surface (Blount and Bloxam). This property of attacking silicates as well as metals makes it necessary to preserve it in lead, platinum, gutta percha, or ceresin coated vessels. In determining the density Zellner made use of a hard rubber pyknometer, or for less accurate work, a westphal balance device with the bob coated with a layer of pitch.

I found (particularly in Gmelin-Kraut) a number of special methods for the analysis of fluorids, and a very complete list of references, but the only one of which I made any use was the simple titration with standard normal alkali, using phenol phthalein as indi-

cator, method described by Winteler (see his reference in Gmelin-Kraut or in Landolt and Bornstein) This method is described in Coblentz-Vousik, page 82. The volumetric solution is half normal alkali free from CO_2, indicator phenol phthalein. Measure out the acid with a waxed pipette into a platinum dish, add excess of standard alkali, heat to boiling, add the indicator, and titrate back with standard half normal sulphuric acid.

In titrating hydrofluosilicic acid, a half alcohol solution is used and the titration carried out according to the equation

H_2SiF_6 plus $2KOH$ = K_2SiF_6 plus $2H_2O$.

Sodium hydroxid forms a hydrolyzable salt with H_2SiF_6 and cannot be used for titration (Coblentz-Vousik)

Sutton, (page 109) says regarding the titration of HF,- "In the case of pure acid..... the reaction when phenol phthalein is employed is very sharp. When however commercial acid is thus titrated, a difference is observed; the pink color obtained on adding the alkali only endured for a second or so and then fades away,

and this may be repeated for some time till at last a permanent pink is produced. The cause of this is silicofluoric acid. The first appearance of pink ensues when the reaction

H_2SiF_6 plus K_2O = K_2SiF_6 plus H_2O

occurs. Then another reaction sets in,

K_2SiF_6 plus $2K_2O$ = $(KF)_6$ plus SiO_2

but from the slight solubility of the K_2SiF_6, some time elapses before it is complete. He says further that this potassium salt furnishes a basis for analysis in determining the H_2SiF_6 content,- in the following manner.

Excess potassium acetate is added to precipitate the salt,- it being insoluble in a mixture of methylated spirit and water. Let stand several hours, wash with a mixture of half spirit and half water, and titrate according to the following equation

K_2SiF_6 plus $2K_2O$ = $(KF)_6$ plus SiO_2.

Haga and Osaka state that the titration of hydrofluoric acid is more affected by carbon dioxid than the titration of other mineral acids. They state further, regarding indicators that

phenol phthalein is the best, rosolic acid almost equal, while litmus, lacmoid and phenacetolin can be used in the hands of an experienced operator. Methyl orange is useless.

Sutton gives also methods for the estimation of sulphuric acid and sulphurous acid.

With the information collected thus far, I built an apparatus after the type described for the manufacture of HF and began its examination. (examination of the acid). My apparatus was entirely of lead, with a single condenser or absorption tower twenty two inches high by five inches diameter. A charge of 300 grams of common fluor spar and 210 c.c. of H_2SO_4 was thoroughly stirred and placed in the retort. With the application of a low flame a generous evolution of gas took place; the most of this I absorbed by repeatedly pouring water into the top of the lead tower. In order to obtain acid of the necessary strength I poured the same water repeatedly through the tower, noting the gain in strength by specific gravity readings.

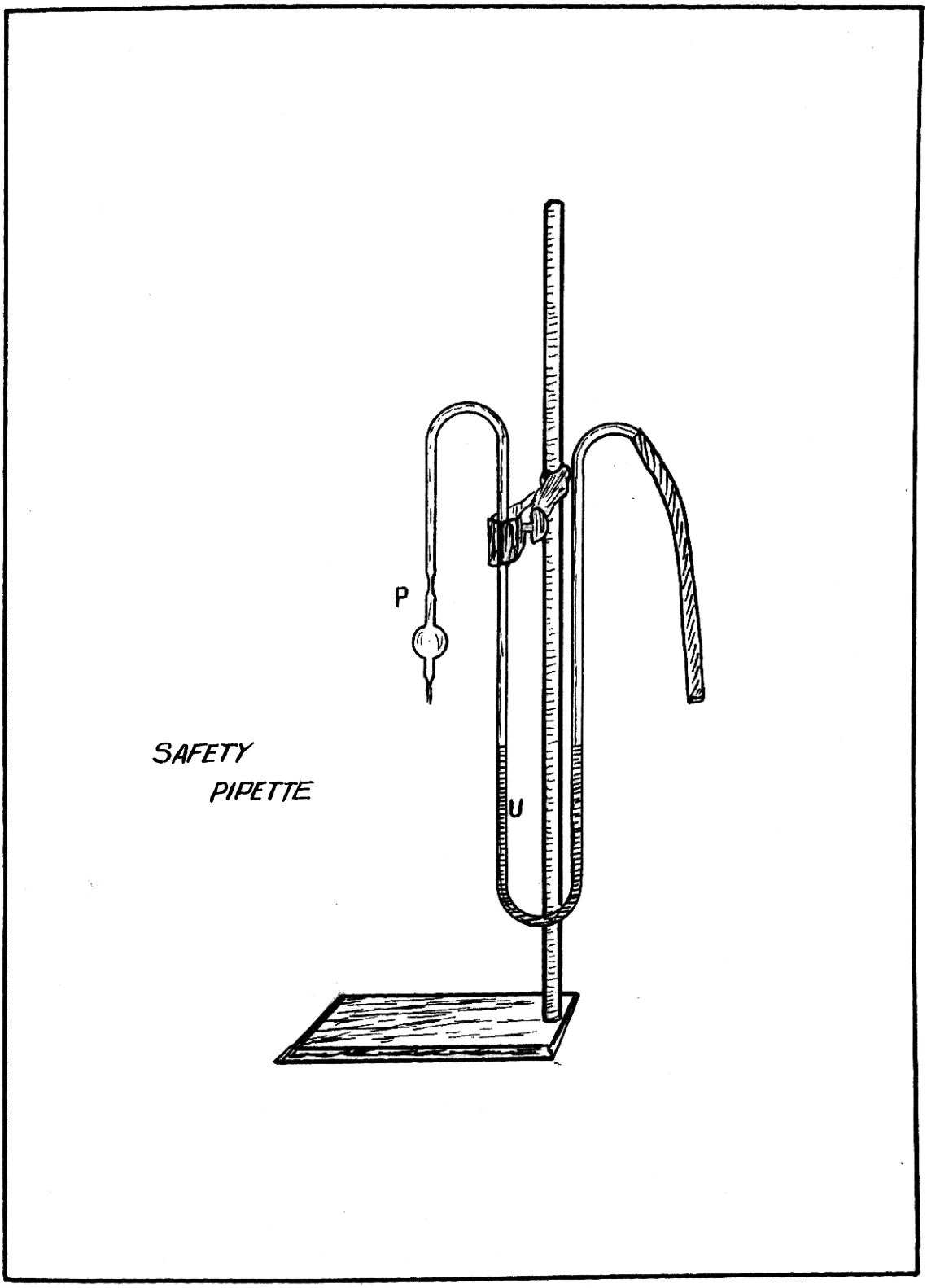
Next I charged the retort with the special

fluor spar and generated a supply of the special acid. These samples were preserved in ceresin or wax bottles for several hours until examination.

The examination consisted of specific gravity determination and the acidity as indicated by normal KOH and normal NaOH, this at several dilutions for each sample of acid. The samples of acid were three:- (a) Baker and Adamson's C.P. hydrofluoric acid, (b) commercial acid made from ordinary fluor spar, (c) commercial acid made from the special fluor spar.

At first I used a westphal balance with waxed bob to determine specific gravity, but made no correction for the increase in volume due to wax or paraffine. This I afterward found to be exceedingly inaccurate, and replaced by a device which I will describe in detail.

A glass pipette shown at "P" connected at its upper end with "U" a safety trap, and at the other end of the safety trap a rubber tube was attached with which to suck up the acid or water into the pipette. The small amount of



SAFETY
PIPETTE

water in the trap prevented any possibility of vapor or liquid HF coming into the mouth, and a coating of paraffine inside the pipette protected it from etching. The pipette was never standardized for volume, but was used as the unit of volume throughout all the work. A pyknometer used also in the determination of specific gravity was a very small hard rubber vessel with a screw top. Into this was put one pipette full of water, weight of water determined; then one pipette full of HF, and its weight obtained. Dividing weight HF by weight H20 gave specific gravity directly, and with an accuracy of 0.1 % and better. The acid from the pyknometer was washed into a waxed beaker and titrated. Data for all standardizations and titrations,* together with the specific gravities of each are as follows:

Standardization of Alkalies with Oxalic acid.

		Wt. Oxalic	Vol. NaOH.
Weighing bottle	20.6816		
again	18.4223	2.2593	34.30
again	16.3992	2.0231	30.81

(1) 1 c.c. NaOH= .065606 = .0208087) gms HF
(2) 1 c.c. NaOH= .065663 = .0208268) per cc.
average = .020822

*Except calibration of burettes.

		Wt. Oxalic	Vol. KOH.
Weighing bottle	16.3996		
again	14.5057	1.8939	36.8
again	12.7729	1.7328	33.9

(1) 1 c.c. KOH= .05146 = .0163298) gms HF
(2) 1 c.c. KOH= .05130 = .016279) per cc.
average = .0163

(burette corrections on the above nil)

For standardization of pipette:

Pyknometer	(1)	(2)	
Empty	11.4695	11.4694	gms
Full of water	14.5575	14.5555	
Water	3.0880	3.0861	avg. 3.087

On Baker & Adamson C.P. HF.

(1) Pyknometer full 15.0722
tare 11.4694
Wt of HF 3.6028 ---Sp. G. 1.168

(2) NaOH
78.58 c.c.
78.55 corrected
= 45.40% acid.

(3) KOH
99.75 c.c.
99.67 corrected
= 44.8% acid

After first dilution

Pyknometer	(1)	(4)	(5)
full	14.9794	14.9935	14.9930
tare	11.4694	11.4694	11.4694
Wt of HF.	3.5100	3.5241	3.5236
Specif. Grav.	1.137	1.142	1.1415

(3) NaOH
67.92 c.c.
67.89 corrected
= 40.15 % acid

(2) KOH
86.70 c.c.
86.65 corrected
= 40.15% acid.

After Second Dilution

Pyknometer	(1)	(4)	(5)
Full	14.8976	14.9045	14.9056
tare	11.4694	11.4694	11.4694
Wt. of HF.	3.4282	3.4351	3.4362
Specif. Grav.	1.110	1.112	1.112

NaOH

(2) 53.23 cc.
53.19 corrected
= 32.25% acid

KOH

(3) 67.90 c.c.
67.87 corrected
= 32.26% acid

On acid made from the common spar

Pyknometer	(1)	(4)
Full	14.9743	14.9690
Tare	11.4694	11.4694
Wt of HF.	3.5049	3.4496
Specif. Grav.	1.1365	1.134

NaOH

(3) 56.95 c.c.
56.91 corrected
= 33.85% acid

KOH

(2) 70.10 c,c.
70.07 corrected
= 32.61% acid

Diluting the same acid

Pyknometer	(1)	(4)
Full	14.8820	14.8837
Tare	11.4694	11.4694
Wt of HF	3.4126	3.4143
Specif. Grav.	1.105	1.106

NaOH

(2) 46.01 c.c.
45.97 corrected
= 28.04% acid

KOH

(3) 57.70 c.c.
57.66 corrected
= 27.53% acid
passed end point
so repeated it.
(5) 56.80 c.c.
56.76 corrected
= 27.11% acid.

Next I added pure silica to C.P. HF shook well and after allowing to stand for five minutes,

Titrated as follows

Pyknometer	(1)
Full	15.1724
Tare	11.4694
Wt of HF	3.7030
Sp. G.	1.200

	NaOH		KOH
(2)	76.12 c.c.	(3)	86.50 c.c.
	76.09 corrected		86.45 corrected
	= 42.76% acid		= 38.02% acid

Diluting the same

Pyknometer	(1)
Full	15.0023
Tare	11.4694
Wt of HF.	3.5329
Sp. G.	1.145

	NaOH		KOH
(2)	60.30 c.c.	(3)	74.10 c.c.
	60.26 corrected		74.07 corrected
	= 35.51% acid		= 34.19% acid.

On acid made from the special spar

Pyknometer	(1)
Full	15.0159
Tare	11.4694
Wt of HF	3.5465

	NaOH		KOH
(2)	62.40 c.c.	(3)	75.65 c.c.
	62.36 corrected		75.62 corrected
	= 36.61% acid.		= 34.75% acid.

And finally as a check to see that the alkalies had not changed since standardization I made up at random a hydrochloric acid solu--

tion and titrated as though it were HF

One pipette of this acid against:

NaOH	KOH
24.41 c.c.	31.19
24.42 corr.	31.20 corrected
corresponding to HF	
36.35% acid	36.32% acid.

This showed that the two alkalies were of the same strength relative to each other as at the beginning of the titrations and at the time they were standardized.

Finally to correlate all my results and compare them, I plotted on cross section paper specific gravity against percent strength for six sets of data:

(1) Winteler's standard tables. (1902)

(2) Eckelt's standard table (1898)

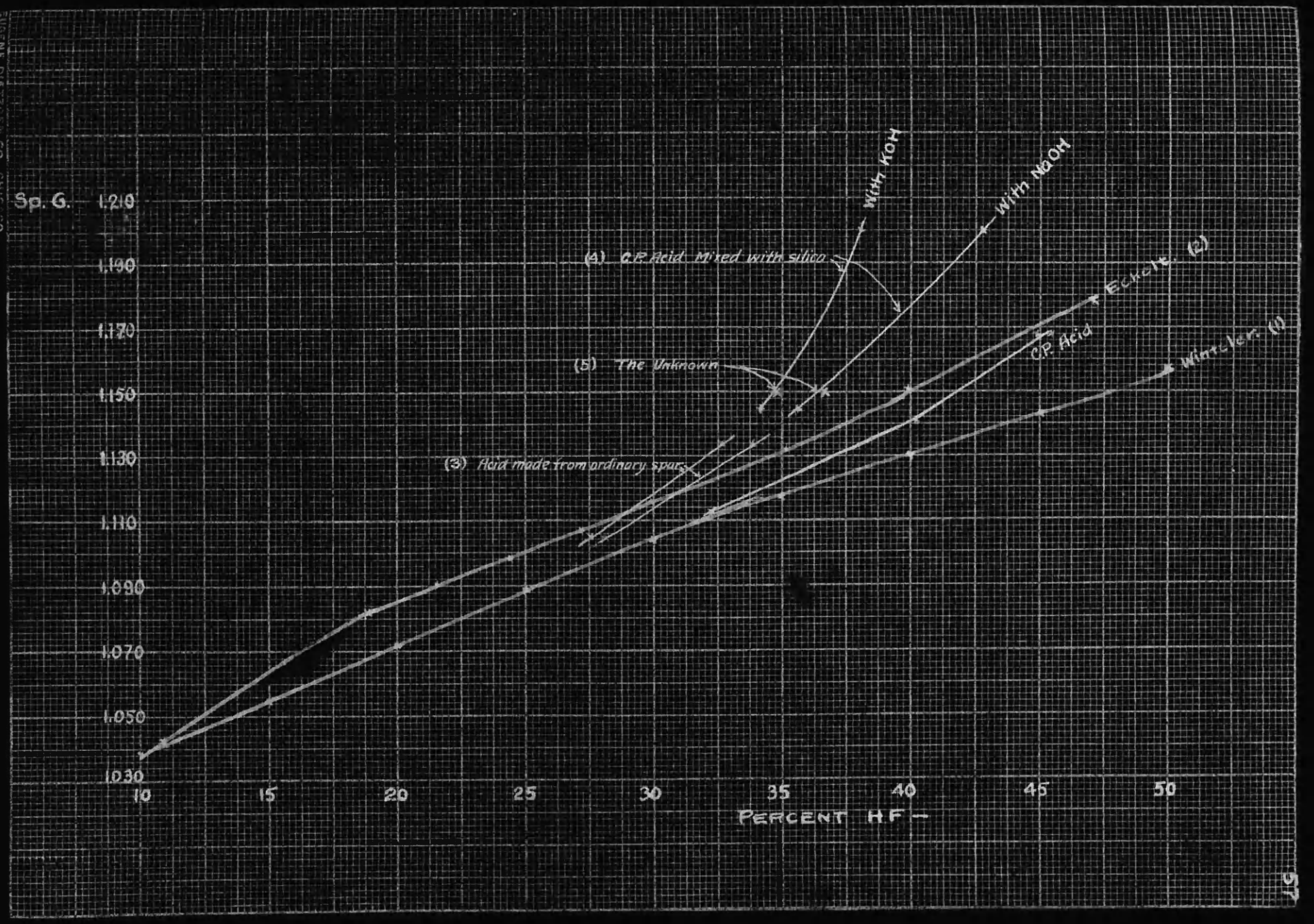
(3) My results from C.P. acid.

(4) My results from acid C.P. mixed with pure silica.

(5) My results from acid made from ordinary fluor spar.

(6) My results from acid made from the special fluor spar.

This table shows several remarkable things: Winteler and Eckelt, the only two authorities, offer widely variant results,- a fact which I am at a loss to explain. I would suppose, however, that Winteler's were the more reliable of the two.


Sp. G.
1.210
1.190
1.170
1.150
1.130
1.110
1.090
1.070
1.050
1.030
10
15
20
25
30
35
40
45
50
PERCENT HF
With KOH
With NaOH
(4) C.P. Acid Mixed with silica
(5) The Unknown
(3) Acid made from ordinary spar
C.P. Acid
Eckelt (2)
Winkler (1)

My results for C.P. acid fall between the two, but give indication that if carried out for dilute solutions, would almost coincide with Winteler's. My results for the unknown, for acid made from ordinary spar, and for the pure acid diluted with silica or hydrofluosilicic acid, coincide exactly, but vary from the C.P. in this particular:- that it requires less KOH than NaOH to neutralize at any one specific gravity,-

This difference in NaOH and KOH titrations is much more noticeable in solutions of high concentrations, and approaches zero in the vicinity of 15% acidity.

Apparently the difference is due to silica, in what way I am not certain, but it is certain that there is a potassium salt of H_2SiF_6 which is less soluble than the corresponding sodium salt. The presence of this salt was indicated by the fact that KOH titrations were longer in reaching the end point than those with NaOH, and that toward the end of a KOH titration a decided tendency to turn, then to fade repeated-

ly was always noticed in silica-bearing acid. It seems that this salt (entirely insoluble in mixtures of half alcohol and half water) forms the basis of a method of analysis. Its presence is further indicated by the fact that the difference is almost unnoticeable in very dilute solutions, where we might expect it to go into solution; and verified by the fact that the sodium hydroxid titration seems to give results much nearer to the correct (Winteler's and Eckelt's) than the potassium alkali.

There is yet one possibility which I did not consider in the work,- the effect of carbon dioxid in the water at any point. It doubtless has a distinct effect,- but what that may be, I cannot say, and for lack of time I was not able to determine.

Now the only way in which this difference could have caused such an effect as Enequist reported is this:- That in the beginning he prepared tables of acidity corresponding to each specific gravity, using as his basis KOH; and that now, when he titrates he uses NaOH.

This is possible but highly improbable, because by no ordinary means could he get acid of more than 35 or 40% strength.

One by one the first five of the six possible explanations of Enequist's problem have been taken up, investigated, and cast out. The sixth reads as follows: "That he had used an entirely different method of determining the percentage strength of his acid, one of which I know nothing, and one which is considerably influenced by one or more of the impurities in the acid." I believe that this is the answer, and my opinion is strengthened by a statement in a recent letter from Liddell that there is a method for determining HF based on its etching strength. He says that it is used to a limited extent by a few manufacturers and users, but he knows nothing further about it.

Now it is very easy to suppose that the etching strength would be a somewhat flimsy basis, and that this etching strength would be easily influenced by impurities. For example silica bearing acid might show a certain acidity, another sample free from silica would show the

same acidity with NaOH, but the pure HF would be much superior as an etching agent. Of course the matter of specific gravity would complicate it, but the effect would exist.

If I could have gotten detailed information along the line suggested by Liddell's statement, I am sure that the sixth could have been shown the correct explanation.